PYROLYSIS OF A HYDROGENATED COAL LIQUID

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Introduction.

The present work forms part of an effort at Stone & Webster
to assess how the production of olefins might be affected by
changes in feedstock origin from petroleum to coal. In what
follows, we focus on experimental results concerning the
characterization, hydrogenation, and pyrolysis of a coal-derived
liquid; for comparison, data are also presented for the pyrolysis
of a petroleum distillate, having a boiling range and hydrogen
content similar to those of the coal liquid, as well as for
pyrolysis of decahydronaphthalene, a model alicyclic substrate.
Some economic implications of these results will be reported
separately; related work in progress includes theoretical and
experimental study of alicyclic pyrolysis pathways.

Sample Preparation and Characterization.

Our investigation commenced with a sample of 'Synthoil' coal
liquid, produced from a Kentucky hvAb coal by a USBM process
recently described by Akhtar et. al. (1). The Synthoil coal liquid
was separated into seven fractions by refluxed batch distillation
at subatmospheric pressures, of order 10 mm Hg. The second fraction
(abbr. CLF), with atmospheric boiling range from 250 C to 380 C,
comprised 36 weight percent of the original sample and this fraction
was catalytically hydrogenated to yield the hydrogenated coal
liquid sample (abbr. HCL) finally pyrolysed.
The coal liquids were characterized by standard analytical
procedures, with application of the SARA separation technique (2)
to enhance mass-spectrometric analyses. The principal SARA
classification categories are Saturated hydrocarbons, Aromatic
hydrocarbons, Resins, and Asphaltenes, with some further sub-
divisions, e.g., mono-, di-, tri-nuclear aromatic hydrocarbons.
Pertinent results are presented in Table 1, (a) elemental analyses,
and (b) SARA separation data. Individual compounds detected in the
hydrocarbon fractions of the Synthoil coal liquid sample appeared
to possess predominantly the pyrene and phenanthrene types of
skeleta; the number of aromatic rings per molecule averaged two,
i.e. the naphthalene type of pi-electron system, with a range from
zero (alicyclic) to five (benzopyrene). It is noteworthy that coal
liquids derived from other catalytic coal conversion processes (3)
also show a preponderance of compounds with pyrene and phenanthrene
structures.

Catalytic Hydrogenation.

The coal liquid fraction, sample CLF, was catalytically
hydrogenated in two stages, with operation temperature, hydrogen
partial pressure, LHSV, respectively (350 C, 125 bar, 0.25 inv. hr)
and (300 C, 125 bar, 0.50 inv. hr). The first stage employed a
presulfided nickel-tungsten catalyst on alumina, a formulation of

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the type commonly used in hydrogenation of aromatic feedstocks. Although detailed intermediate analyses were not obtained, it is estimated that the first stage reduced the aromatics content of the coal liquid from about 75 wt % to about 25 wt %. The second stage employed a proprietary catalyst formulation which included a Pt group metal carried on alumina; this further reduced the aromatics content to about 12 wt %, its final value.

Approximate analyses of the coal liquids before and after hydrogenation are indicated by Table 2, in terms of a matrix of the major compound types detected. Each row in Table 2 represents a particular structural skeleton, while each column represents a particular aromatic nucleus; carbon numbers increase from the bottom upwards and the extent of hydrogenation increases from left to right. Each element of the matrix is labelled by the structure of the compound, and by two numbers representing the respective weight percentages of that compound in the coal liquid samples before (CLF) and after (HCL) hydrogenation. Table 2 shows clearly the predominance of pyrene and phenanthrene structures in both the CLF and HCL samples. The total amount of 3-ring compounds was approximately the same, $\simeq$ 40 wt %, before and after hydrogenation but compounds with $\geq$ 4 rings seemed to decrease while those with $\leq$ 2 rings increased following hydrogenation, suggestive of some associated hydrogenolysis. It should also be noted that the aromatic compounds remaining in the hydrogenated coal liquid were mainly benzenes substituted with alicyclic structures.

Pyrolysis Experiments.

The pyrolysis experiments were conducted in an electrically-heated once-through tubular flow reactor, designed to simulate the time-temperature history experienced in commercial steam-cracking operations. Reactor effluent compositions were ascertained by gas-chromatograph and mass-spectrometer analyses. Three feedstocks were pyrolysed: the hydrogenated coal liquid sample (HCL) described earlier, a petroleum distillate (LGO), of Kuwaiti origin, and decahydronaphthalene (DHN) of 99.99 wt % purity with cis-trans isomer percentages 47-53.

Pyrolysis results are summarized in Table 3, parts (a), (b), and (c) of which respectively concern feedstock characterization, pyrolysis conditions, and product yields.

Comparison of HCL and LGO feedstocks in Table 3(a) reveals substantial similarities in their physical properties, i.e. specific gravity and distillation data, but striking contrasts in chemical constitution, the respective paraffin, alicyclic, aromatic contents being HCL(1.0, 83.1, 12.8) and LGO(56.9, 23.0, 20.1). Pronounced differences also exist within each of the respective alicyclic and aromatic roups. Thus the HCL contains mainly 3-ring alicyclics lacking side chains, while the LGO has mainly single ring alicyclic compounds with substantial aliphatic side chains. Single aromatic ring compounds dominate the aromatic fractions in both the HCL and LGO but the benzene ring substitutions differ, the HCL containing cata-condensed alicyclic substituents, e.g. octahydrophenanthrene, whereas the LGO contains open chain alkyl substituents, e.g. n-octyl benzene. The HCL characterization suggests that it should be well modelled by an alicyclic compound of 2 to 3 rings, i.e., decahydro-naphthalene or perhydrophenanthrene. Table 3(a), column 3 shows that the DHN specific gravity and hydrogen content are indeed very

close to those of the HCL.

All three feedstocks were pyrolysed under substantially similar conditions, given in Table 3(b), with steam to hydrocarbon weight ratios 0.75±0.25, reactor residence times 0.35±0.05 sec, exit pressures 1.80±0.05 bar, and exit temperatures 862±12 C.

Pyrolysis product spectra, shown in Table 3(c), merit comparisons between the HCL and LGO, and also between the HCL and DHN feedstocks.

Relative to the LGO, the HCL yielded somewhat less ethylene, and about half the propylene. Yields of 1,3 butadiene were about equal in both cases, but the HCL yielded only half the butenes, making for a greater proportion of the butadiene in the C4 fraction. In the aromatic 'BTX' fraction, the HCL produced roughly twice as much of each component, the ratio of C6:C7:C8 aromatic compounds being approximately the same 1.0:0.5:0.25 for each feedstock. The pyrolysis fuel oil fraction, with atmospheric boiling point $\geq$ 205 C, was approximately equal in each case. The respective fuel oil samples were both aromatic, had similar hydrogen contents of 6.85±0.15 wt %, and analogous Rayleigh distillation curves, but differed in chemical constitution, the fuel oil from HCL containing major amounts of pyrenes and phenanthrenes whereas naphthalenes were the predominant constituents, $\approx$ 47 wt %, of the fuel oil from LGO.

Product yields from the HCL and DHN feedstocks showed striking similarities, the yields of compounds from hydrogen through to the C5 fraction being virtually identical. Total BTX yields from HCL and from DHN were roughly in the ratio 2:3, with proportions of the C6-C8 aromatic compounds the same in each case. The HCL yielded twice as much pyrolysis fuel oil as DHN. The respective fuel oil samples were both aromatic, and had similar hydrogen contents and distillation curves, but their chemical compositions differed, the sample from DHN containing a broad distribution of aromatic compound types with naphthalenes, $\approx$ 15 wt %, somewhat more abundant than any other group.

Discussion.

Hydrocarbon pyrolysis involves mainly free radical and pericyclic types of reactions, the principles of which are known well enough (4,5) to permit inference of likely pyrolysis pathways for any given molecule. Two simplified examples, pertinent to the present experiments, are illustrated in Figure 1, which shows a plausable pathway for each of (a) perhydrophenanthrene and (b) octahydrophenanthrene, these compounds being respectively representative of the alicyclic and aromatic constituents of the HCL sample. The pathway in Figure 1(a) commences in classical Rice-Herzfeld fashion, with hydrogen abstraction from the 10 position; the resulting radical undergoes three successive beta C-C bond scissions and a final hydrogen atom elimination, leading to the 'primary' unsaturated products of ethylene, 1,3 butadiene and 1,3,5 hexatriene. The hexatriene is unstable relative to its 1,3 cyclohexadiene isomer, the pericyclic pathway shown proceeding through electrocyclic ring closure of a butadiene moiety to cyclo-butene, followed by a 1,3 sigmatropic alkyl migration (alternately, the hexatriene could isomerize to the all-cis form which undergoes

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electrocyclic ring closure). Finally, 1,3 hexadiene pyrolysis
leads to benzene in high yields (6), by a radical mechanism. The
pathway in Figure 1(b), with an aromatic substrate, starts with
hydrogen abstraction from the 2 position; this leads to a radical
in which beta scission either requires rupture of the strong 1-11
bond or forms a non-propagating benzylic radical at the 4 position,
making hydrogen atom elimination a likely alternative. The molecule
produced now contains a 1,4 dihydronaphthalene moiety, which is
prone to pericyclic group transfer (1,4 elimination) with formation
of the corresponding naphthalene moiety. This type of pathway will
evidently cause any originally hydro-aromatic substrate to revert
to its fully aromatic analog.
     Application of the foregoing provides some insight into the
product yield spectra resulting from the HCL, LGO, and DHN
feedstocks. In regard to the appreciably lower propylene yields
obtained from HCL (also DHN) relative to LGO, we note that propylene
is primarily produced by beta scission from 4-carbon moieties of
the n- and iso-butyl type, following H abstraction from the 2 and
1 (or 1') positions respectively. Such moieties are abundant in
normal- and iso-paraffin compounds, which comprise a major portion
of the LGO feedstock, but are absent in alicyclic structures,
which predominate in the HCL. Incidentally, the propylene yield
from the HCL is far from negligible because pyrolysis of the primary
substrate molecules produces others which contain the requisite
moieties; e.g. in Figure 1(a), the primary radicals formed after
steps 3 and 6 could each abstract hydrogen from the substrate, with
the resulting molecules both containing n-butyl moieties. There
are two possible reasons why the ethylene yield from HCL was lower
than that from LGO. First, at the present experimental conditions,
appreciable amounts of ethylene arise from propylene decomposition,
with reduced yields of such 'secondary' ethylene a consequence of
the observed lower propylene yields. Second, the aromatic molecules
in the LGO probably contribute more ethylene than those in the HCL.
Ethylene production from substituted aromatic molecules requires
alkyl carbon atoms more than two sigma bonds distant from the
aromatic ring periphery, e.g., n-octyl benzene contains six such C
atoms whereas 1,2,3,4,5,6,7,8 octahydrophenanthrene contains none.
It had earlier been pointed out that the aromatics in LGO included
alkyl benzenes, whereas those in the HCL were akin to octahydro-
phenanthrene. The BTX fraction is another major product of both
HCL and LGO pyrolyses. The relatively greater amount of benzene,
and associated C7 and C8 benzenes, obtained from the HCL seems
related to the tendency of polynuclear alicyclic compounds to yield
vinyl butadienes as primary pyrolysis products which can then follow
facile pathways via hexadiene to benzene, possibly along lines
indicated in Figure 1(a). The HCL and LGO produced roughly equal
amounts of pyrolysis fuel oil, the differing chemical constitutions
of which mainly reflect differences in the aromatic portions of the
respective feedstocks.
     The congruence between HCL and DHN product yield spectra for
compounds containing less than eight carbon atoms implies a close
similarity of pyrolysis pathways. Essentially the only difference
arises in the pyrolysis fuel oil yields, in which regard the yield
from DHN might reasonably be considered characteristic of polynuclear
alicyclic pyrolysis under the present conditions. The alicyclic
portion of the HCL would therefore be expected to yield about

$0.85 \times 11.6 \doteq 10$ wt % out of the observed 22.5 wt % fuel oil, the remainder, 12.5 wt %, corresponding closely with the amount of aromatic compounds, 12.8 wt %, in the HCL feedstock. This suggests that the hydro-aromatic compounds present in the HCL were mainly pyrolysed to polynuclear aromatic compounds eventually contained in the fuel oil fraction; it is likely that pathways of the type shown in Figure 1(b) contribute to this conversion.

Finally, the foregoing has two interesting implications concerning catalytic hydrogenation of coal-derived liquids to provide pyrolysis feedstocks. First, the polynuclear aromatic molecules contained in coal liquids must be hydrogenated to their fully alicyclic analogs in order to provide desirable pyrolysis products; partial hydrogenation leads to hydro-aromatic molecules which tend to revert to their fully aromatic form upon pyrolysis, contributing mainly to the relatively undesirable fuel oil fraction. Put another way, the incremental yield of desirable olefinic products increases most strongly as the feedstock aromatics content approaches zero. Second, since the final stages of hydrogenation are of decisive importance, the most appropriate catalysts should be those capable of converting multiply substituted benzenes, i.e., catalysts which are relatively insensitive to the steric effects resulting from substitution around the aromatic ring periphery.

References.

1.   S. Akhtar, N.J. Mazzocco, M. Weintraub, and P.M. Yavorsky, "Synthoil Process for Converting Coal to Non-polluting Fuel Oil." Paper to the Fourth Synthetic Fuels from Coal Conference, Stillwater, Oklahoma (1974).

2.   D.M. Jewell, J.H. Weber, J.W. Bunger, H. Clancher, and D.R. Latham, Anal. Chem. 44, 1391 (1972).

3.   J.T. Swansiger, F.E. Dickson, and H.T. Best, Anal. Chem. 46, 730 (1974).

4.   J.K. Kochi, "Free Radicals," John Wiley & Sons (1973).

5.   R.B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry," Verlag Chemie/Academic Press (1970).

6.   S.W. Benson and R. Shaw, J. Amer. Chem. Soc. 89, 5351 (1967).

Table 1. Analyses of Coal Liquid Samples.

     (a) Elemental Analyses.

Sample	H	C	N	O	S	C/H
	percent by weight					atomic
Coal Source (hvAb, MAF)	5.7	72.7	1.4	13.6	6.6	0.94
Synthoil Coal Liquid	9.07	87.14	0.83	2.06	0.90	1.25
Coal Liquid Fraction 2	10.47	87.50	0.38	1.52	0.13	1.44
Hydrogenated Coal Liquid	12.76	87.14	0.03	0.07	0.001	1.76

     (b) SARA Separation Data

Sample	Satur HC	Arom HC	Resins	Asphaltenes
	percent by weight			
Synthoil Coal Liquid	13.6	37.4	17.7	31.3
Coal Liquid Fraction 2	25.7	62.6	11.7	0.0
Hydrogenated Coal Liquid	84.1	12.8	3.1	0.0

Table 2. Approximate Compositions of Coal Liquid Samples
Before and After Hydrogenation.

1.0 / 0.3					0.9 / 0.0
	2.5 / 0.8	0.6 / 0.0	1.5 / 0.2	4.0 / 1.6	+
	3.1 / 0.4	2.8 / 0.2	7.7 / 0.2	5.0 / 1.9	5.3 / 14.7
		0.4 / 0.0	13.6 / 0.6	16.7 / 4.5	9.6 / 35.0
			1.2 / 0.0	9.5 / 2.5	6.4 / 22.0
				1.1 / 0.0	4.4 / 13.8

Note: Figures in table are percentages by weight of the compound.
In each row, upper figures refer to Coal Liquid Fraction 2
before hydrogenation (sample CLF), while lower figures refer
to Hydrogenated Coal Liquid (sample HCL).

Table 3. Summary of Pyrolysis Experiments.

(a) Feedstock Characterization.

Feedstock Sample*	HCL	LGO	DHN
Specific Gravity, 15/15 C	0.895	0.828	0.883
Elemental Analysis: H wt %	12.76	13.70	13.12
C wt %	87.14	86.16	86.88
Distillation, ASTM D86, vol % vs. deg C			
0 (IBP)	184	193	187
10	245	238	
30	268	271	
50	285	293	191
70	304	318	
90	333	351	
100 (EP)	348	389	196
Hydrocarbon Group Types, wt %:			
n-paraffins	0.0	23.50	0.0
i-paraffins	1.0	33.40	0.0
alicyclics	83.1	23.00	100.0
aromatics	12.8	20.10	0.0

(b) Pyrolysis Conditions.

	HCL	LGO	DHN
Steam/Hydrocarbon weight ratio	1.0	0.5	0.5
Residence time, sec	0.3	0.4	0.35
Reactor exit pressure, bar abs	1.85	1.80	1.75
Reactor exit temperature, deg C	875	854	854

(c) Product Yields, in weight percent.

	HCL	LGO	DHN
Hydrogen	1.03	0.60	1.05
Methane	11.66	12.00	10.35
Acetylene	0.49	0.39	0.54
Ethylene	18.83	22.66	19.36
Ethane	2.40	3.96	2.86
Propadiene, Propyne	0.58	0.41	0.29
Propylene	7.83	13.02	6.57
Propane	0.21	0.34	0.20
1,3 Butadiene	4.68	4.82	4.65
Butenes	1.63	3.12	1.41
C5 olefins, diolefins	2.56	2.72	2.24
Benzene	12.15	6.71	17.97
Toluene	6.76	3.51	10.34
C8 Aromatics	3.43	2.11	4.88
Other C6, C7, C8	0.48	0.50	0.42
C9+ to 205 C	2.82	2.61	5.21
Pyrolysis Fuel Oil ($\geq$ 205 C)	22.46	20.51	11.66
Total	100.00	100.00	100.00

* Feedstock abbreviations as follows:
HCL Hydrogenated Coal Liquid sample.
LGO Light Gas Oil petroleum distillate (Kuwait, desulfurized).
DHN Decahydronaphthalene.

FIGURE 1. Pyrolysis Pathways for Hydrogenated Coal Liquid Constituents.

(a) Alicyclic (Perhydrophenanthrene)

(b) Aromatic (1,2,3,4,5,6,7,8 Octahydrophenanthrene)

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